

Supporting Information

Highly Active PdSb Catalysts on Porous Carbon for Electrochemical Oxidations of Biomass-derived C1- C3 Alcohols

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Table S1. Pd and Sb contents in the Pd/PC and Pd_xSb_y/PC catalysts.

Samples	Pd (wt%) ^a	Sb (wt%) ^a	Total (wt%) ^a
Pd/PC	14.9	0	14.9
Pd _{0.93} Sb _{0.07} /PC	13.8	1.2	15.0
Pd _{0.90} Sb _{0.10} /PC	12.6	1.4	14.0
Pd _{0.85} Sb _{0.15} /PC	12.1	2.2	14.3

^a Determined by ICP spectrometer**Table S2.** BET surface area and pore volume of the carbon materials used as support.

Samples	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
C	165	0.52
AC	215	0.63
PC	630	1.21

Table S3. Electronic parameters of Pd/PC and Pd_{0.90}Sb_{0.10}/PC characterized by XPS and XANES analyses.

Samples	Pd 3d _{3/2} (eV) ^a	Pd 3d _{5/2} (eV) ^a	White line intensity (a.u.) ^b
Pd/PC	340.88	335.58	0.947
Pd _{0.90} Sb _{0.10} /PC	340.58	335.28	0.952

Determined by ^a XPS and ^b Pd K-edge XANES spectra

Table S4. EXAFS fitting results of Pd K-edge for Pd.

Samples	shell	CN	R (Å)	ΔE_0 (eV)	σ^2 (Å ²)
Pd _{0.90} Sb _{0.10} /PC	Pd-O	1.04	2.021	4.12	0.0032
	Pd-Pd	5.95	2.744	-2.74	0.0049
	Pd-Pd	1.43	3.223	-2.74	0.0080
Pd/PC	Pd-O	0.89	2.024	6.323	0.0060
	Pd-Pd	6.64	2.737	-3.48	0.0043
	Pd-Pd	1.19	3.205	-3.48	0.0015
PdO	Pd-O	4.00	2.019	3.29	0.0031
	Pd-Pd	4.00	3.108	9.32	0.0025
Pd foil	Pd-Pd	12.00	2.738	-0.46	0.0044

Table S5. Current density and mass activity of commercial Pd/C, Pd/AC, Pd/PC and Pd_xSb_y/PC in ethanol oxidation.

Samples	Current density (mA cm ⁻²)	Mass activity (A mg _{Pd} ⁻¹)
Pd/C	109.8	1.630
Pd/AC	116.4	1.728
Pd/PC	139.8	2.787
Pd _{0.93} Sb _{0.07} /PC	145.1	3.138
Pd _{0.90} Sb _{0.10} /PC	180.1	4.244
Pd _{0.85} Sb _{0.15} /PC	143.1	3.400

Table S6. Comparison of EOR performances over Pd based catalysts.

Catalyst	Electrolyte	Mass activity (A mg _{Pd} ⁻¹)	Ref.
Pd _{0.90} Sb _{0.10} /PC	1.0 M EtOH + 1.0 M KOH	4.24	This work
Pd/a-SrRuO ₃	1.0 M EtOH + 1.0 M KOH	4.00	S1
Pd ₄₀ Ni ₄₃ P ₁₇	1.0 M EtOH + 1.0 M NaOH	4.95	S2
PdCo@NPNCs	1.0 M EtOH + 1.0 M KOH	1.33	S3
Pd/TiO ₂ -NC	1.0 M EtOH + 1.0 M KOH	2.59	S4
Au ₈₀ @Pd ₂₀ /C	0.5 M EtOH + 0.5 M KOH	0.83	S5
PAG	1.0 M EtOH + 0.5 M NaOH	3.69	S6
Pd/Ni(OH) ₂ /rGO	1.0 M EtOH + 1.0 M KOH	1.55	S7
Pd ₂ Ru/C	1.0 M EtOH + 1.0 M NaOH	2.99	S8
PdCu ₂	1.0 M EtOH + 1.0 M KOH	1.60	S9
Pd/Ru	1.0 M EtOH + 1.0 M KOH	1.15	S10
Pd/C promoted with CaSiO ₃	1.0 M EtOH + 1.0 M KOH	1.5	S11
PtPd(1:3)/RGO/GC	1.0 M EtOH + 1.0 M KOH	1.50	S12
PdC-MoC	1.0 M EtOH + 1.0 M KOH	3.72	S13
Au@Pd NRs	1.0 M EtOH + 1.0 M KOH	2.92	S14
IM-Pd ₃ Pb NNs	1.0 M EtOH + 1.0 M KOH	3.2	S15
Pd ₁ Ru _{0.69} /TiO ₂	1.0 M EtOH + 1.0 M NaOH	2.70	S16
CNT/Pd	1.0 M EtOH + 1.0 M KOH	2.94	S17

Table S7. Mass activity and onset potential of commercial Pd/C, Pd/PC and Pd_{0.90}Sb_{0.10}/PC in methanol, ethanol, ethylene glycol and glycerol oxidation.

Samples		Methanol	Ethanol	Ethylene glycol	Glycerol
Pd/C	Mass activity (A mg _{Pd} ⁻¹)	1.13	1.63	1.25	1.39
	Onset potential (V vs SCE) ^a	-0.412	-0.457	-0.516	-0.369
Pd/PC	Mass activity (A mg _{Pd} ⁻¹)	1.55	2.79	2.01	1.95
	Onset potential (V vs SCE) ^a	-0.408	-0.509	-0.585	-0.362
Pd _{0.90} Sb _{0.10} /PC	Mass activity (A mg _{Pd} ⁻¹)	2.51	4.24	3.18	3.22
	Onset potential (V vs SCE) ^a	-0.460	-0.544	-0.629	-0.398

^a The onset potential was determined at 0.3 A mg_{Pd}⁻¹.

Table S8. Electrochemical impedance parameters of commercial Pd/C, Pd/PC and Pd_xSb_y/PC in 1.0 M KOH + 1.0 M ethanol solution at - 0.3 V vs. SCE.

Samples	R _s (Ω)	R _{ct} (Ω)	CPE (F cm ⁻²)
Pd/C	6.53	211.25	0.000385
Pd/PC	7.05	169.76	0.000418
Pd _{0.93} Sb _{0.07} /PC	6.85	132.44	0.002561
Pd _{0.90} Sb _{0.10} /PC	7.28	72.14	0.001349
Pd _{0.85} Sb _{0.15} /PC	7.22	92.28	0.001226

Reference for Table S7.

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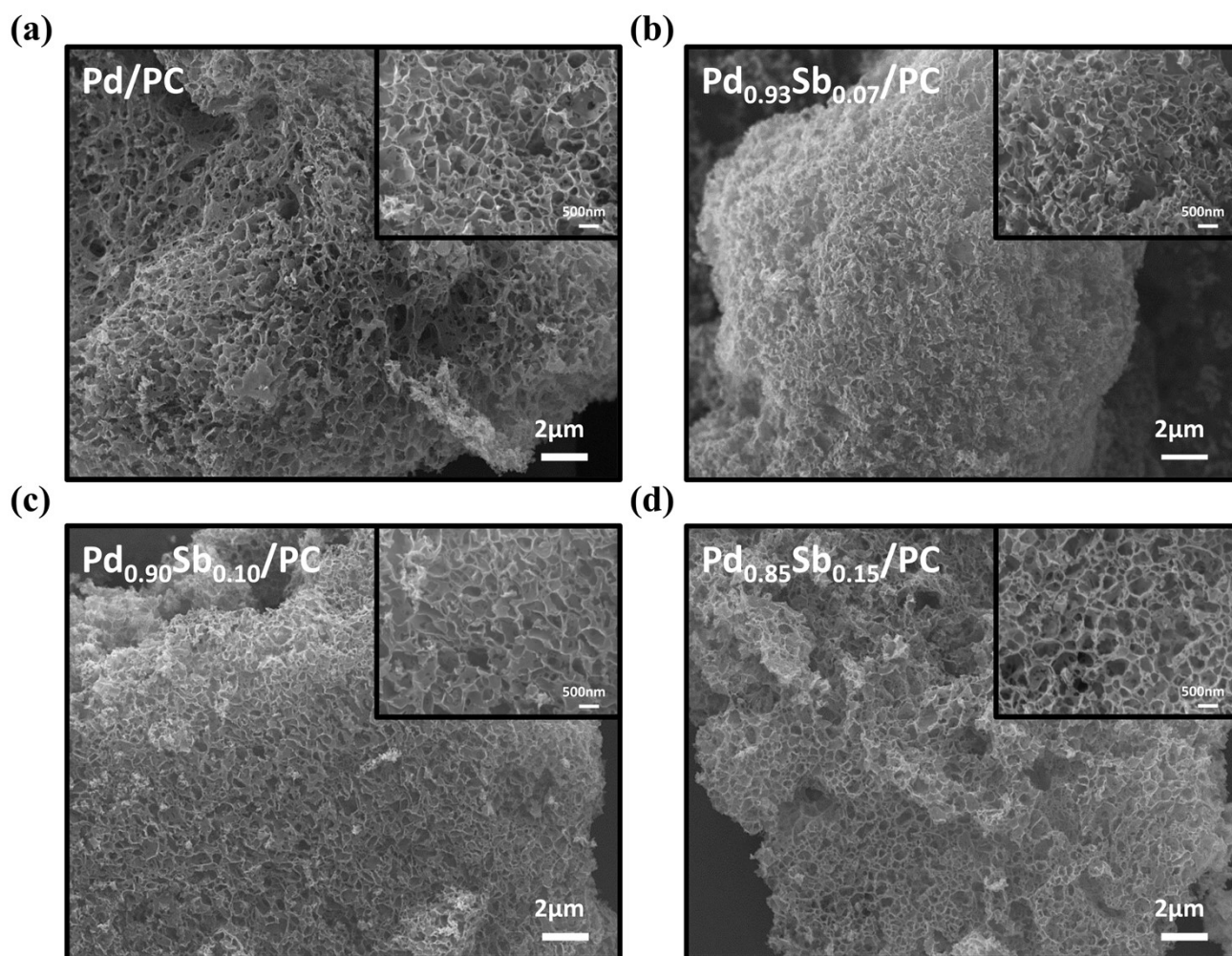


Fig. S1. SEM images of (a) Pd/PC, (b) Pd_{0.93}Sb_{0.07}/PC, (c) Pd_{0.90}Sb_{0.10}/PC and (d) Pd_{0.85}Sb_{0.15}/PC.

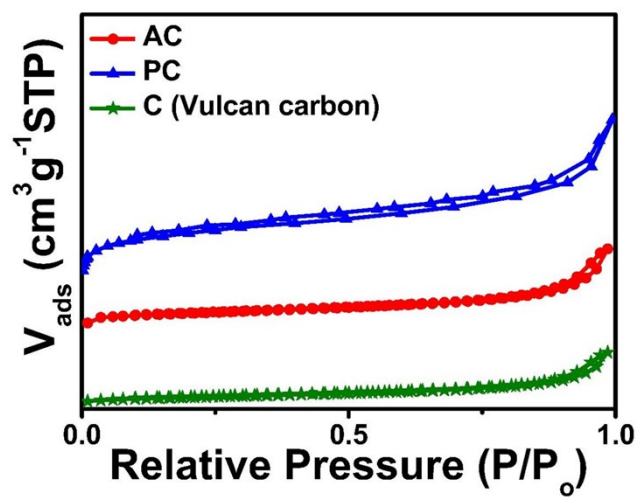


Fig. S2. N_2 adsorption/desorption isotherms for C, AC and PC

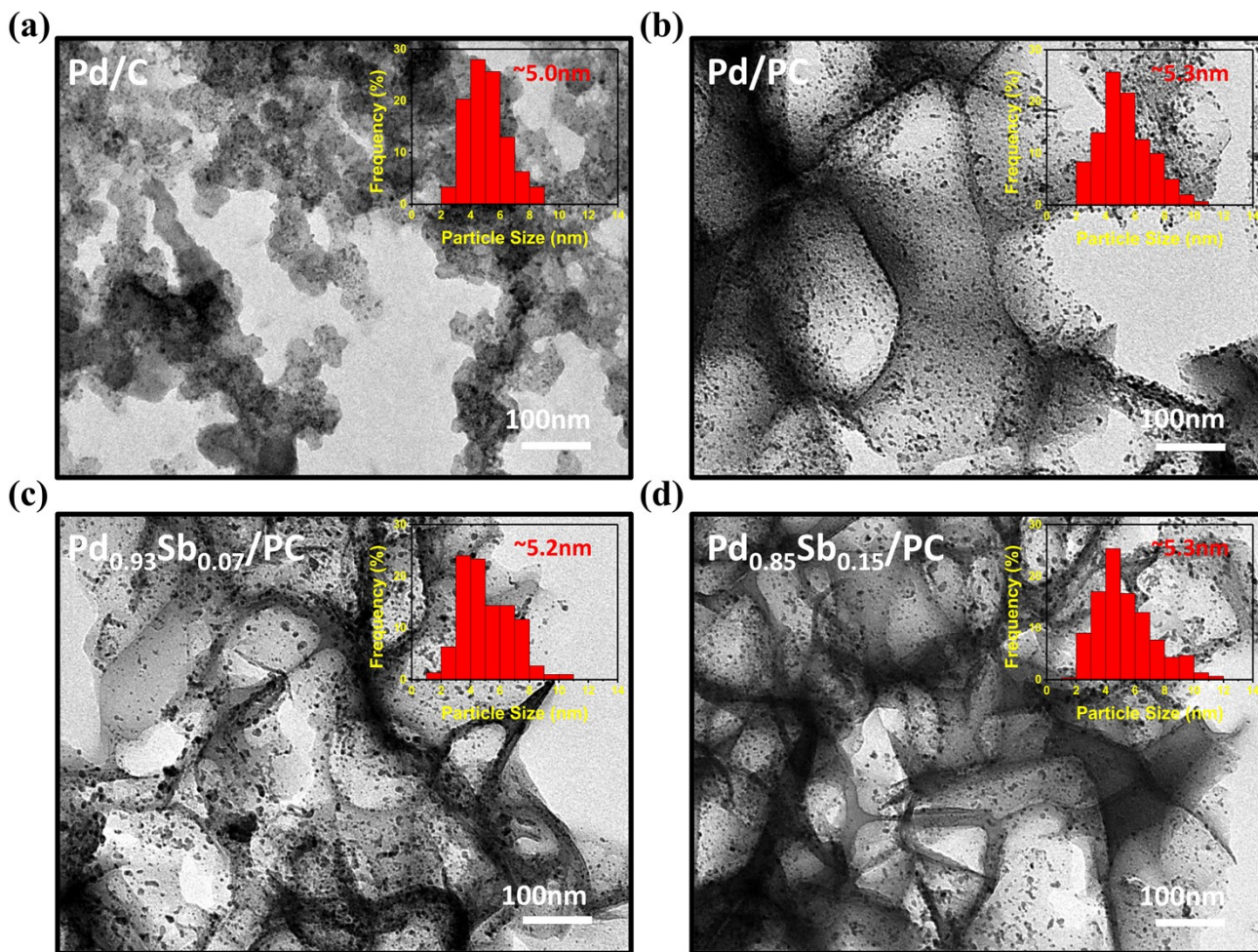


Fig. S3. TEM images and particle size distribution of (a) Pd/C, (b) Pd/PC, (c) Pd_{0.93}Sb_{0.07}/PC and (d) Pd_{0.85}Sb_{0.15}/PC.

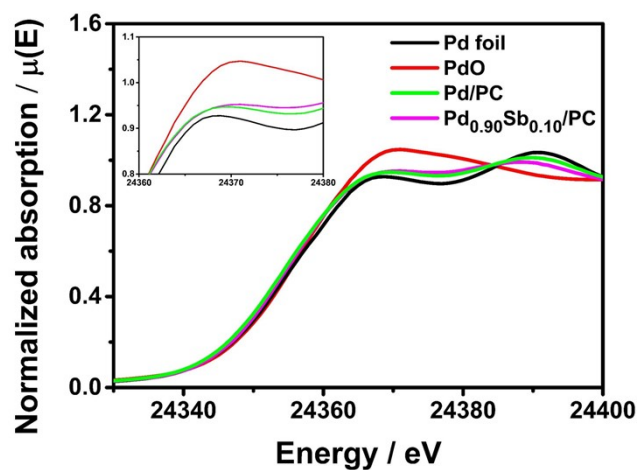


Fig. S4. Pd K-edge XANES spectra for the Pd/PC and Pd_{0.90}Sb_{0.10}/PC with Pd foil and PdO as references. The inset shows a magnified image for white line intensity.

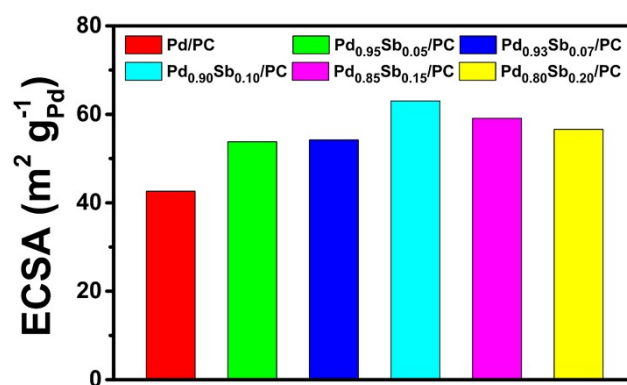


Fig. S5. The values of ECSA for Pd/PC and Pd_xSb_y/PC.

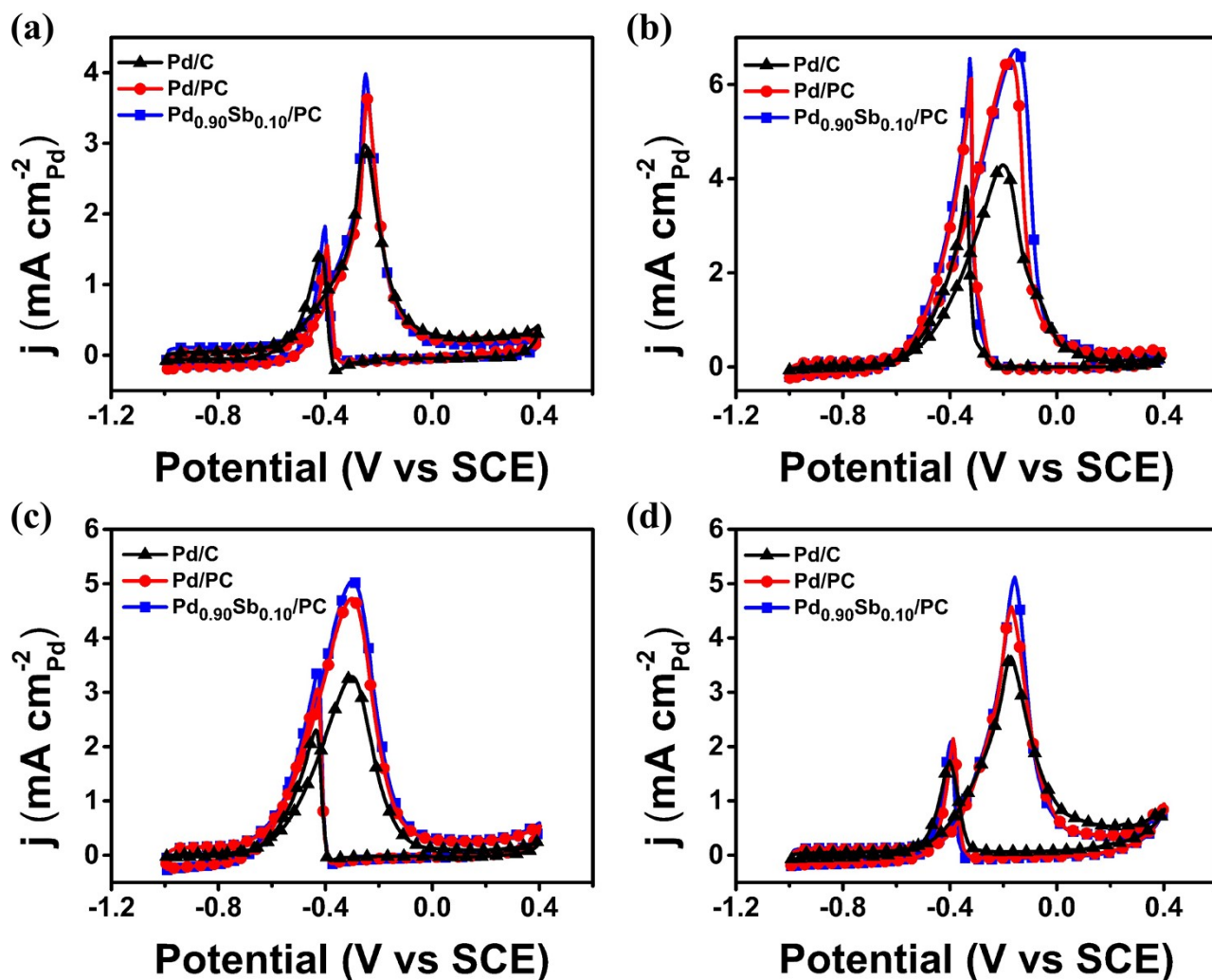


Fig. S6. Specific activities of commercial Pd/C, Pd/PC and Pd_{0.90}Sb_{0.10}/PC in 1.0 M KOH solutions containing (a) methanol, (b) ethanol, (c) ethylene glycol and (d) glycerol, respectively.

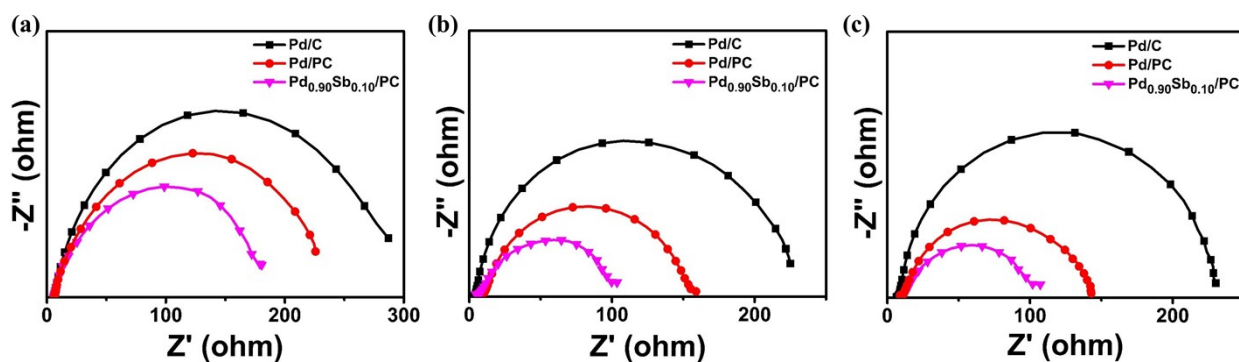


Fig. S7. Nyquist plots at - 0.30 V (vs. SCE) in (a) 1.0 M KOH + 1.0 M methanol solution, (b) 1.0 M KOH + 1.0 M ethylene glycol solution and (c) 1.0 M KOH + 1.0 M glycerol solution.

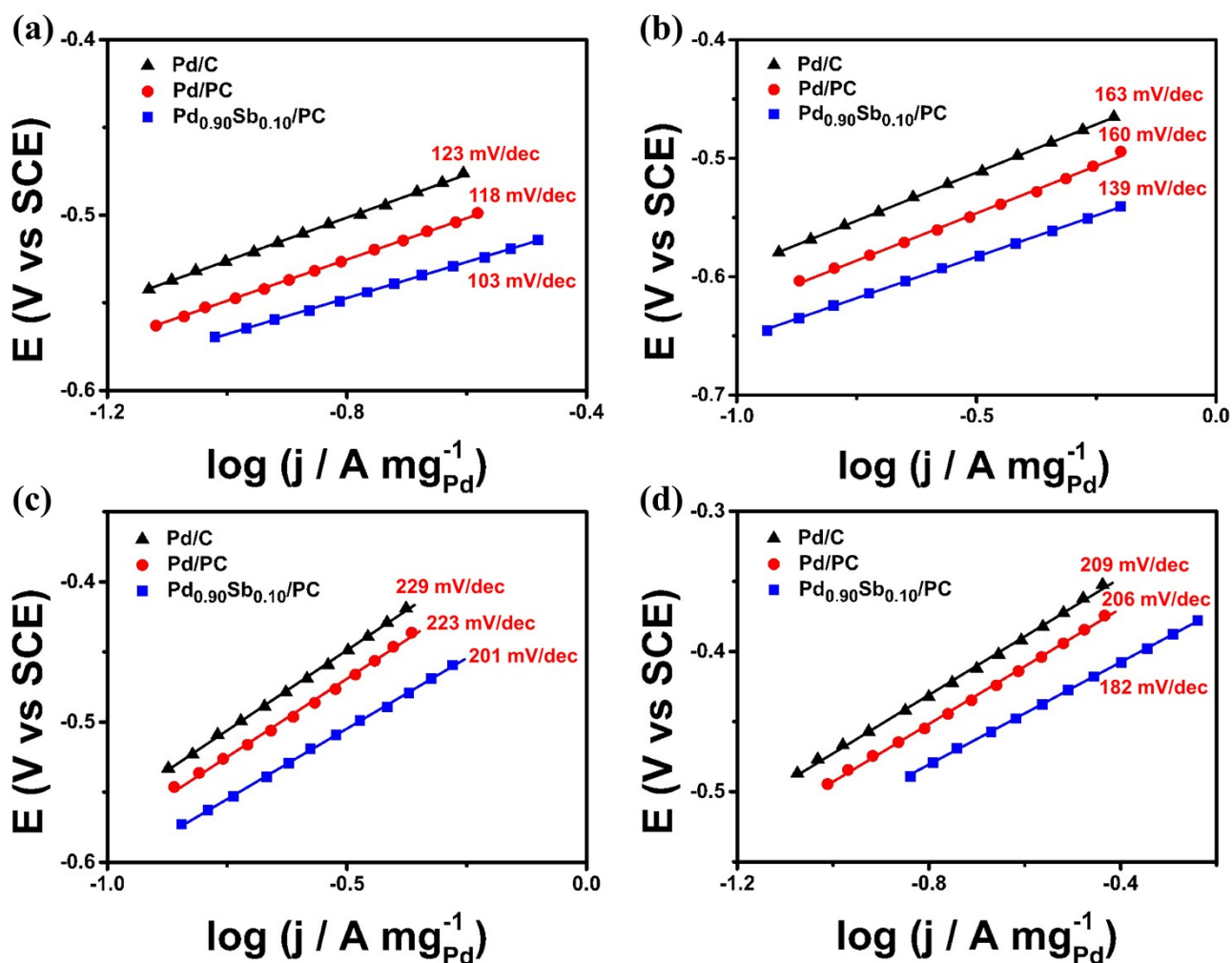


Fig. S8. Tafel plots of Pd/C, Pd/PC and Pd_{0.90}Sb_{0.10}/PC in 1.0 M KOH solutions containing (a) methanol, (b) ethanol, (c) ethylene glycol and (d) glycerol, respectively.

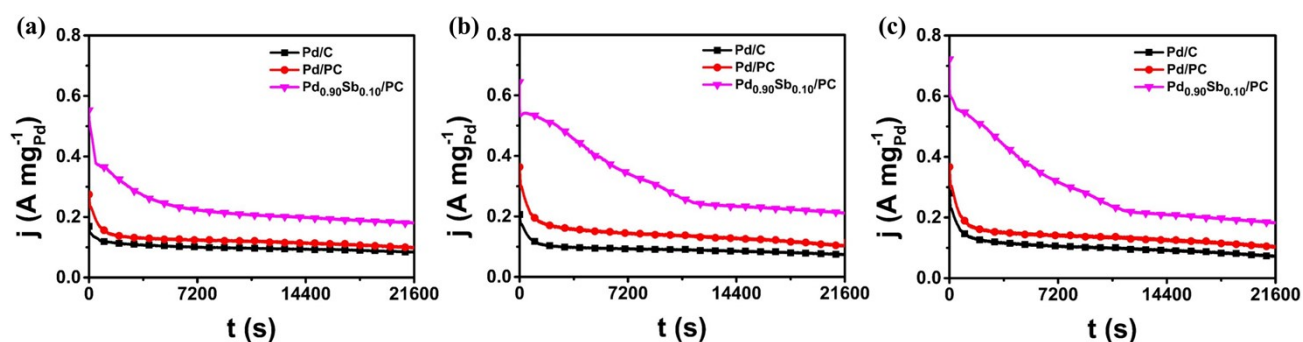


Fig. S9. Chronoamperometric measurements at -0.35 V (vs. SCE) in (a) 1.0 M KOH + 1.0 M methanol solution, (b) 1.0 M KOH + 1.0 M ethylene glycol solution and (c) 1.0 M KOH + 1.0 M glycerol solution.